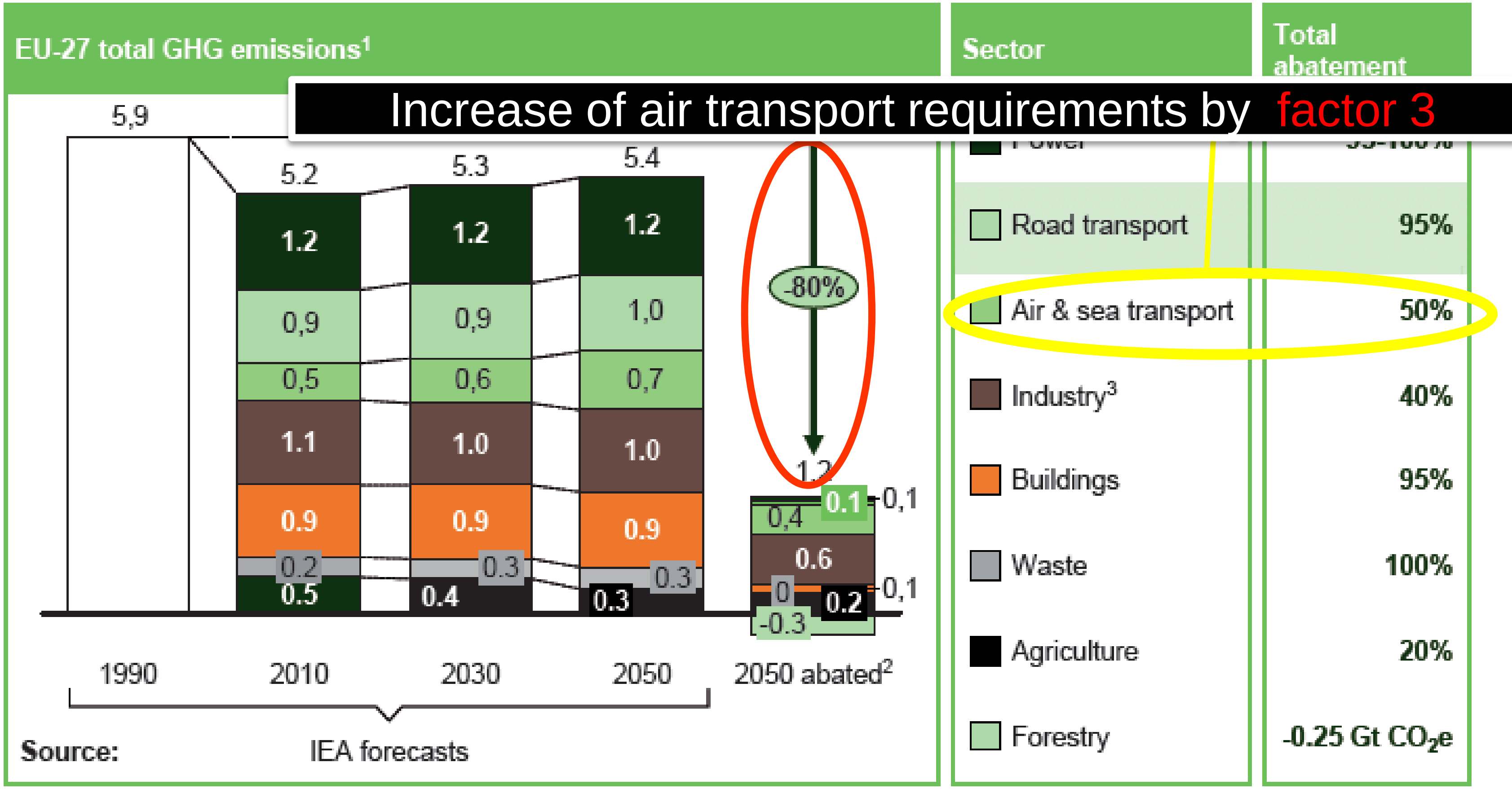
Solar Fuels
Renewable Options Beyond Biofuels

Robert Pitz-Paal, Christian Sattler
Institut of Solar Research

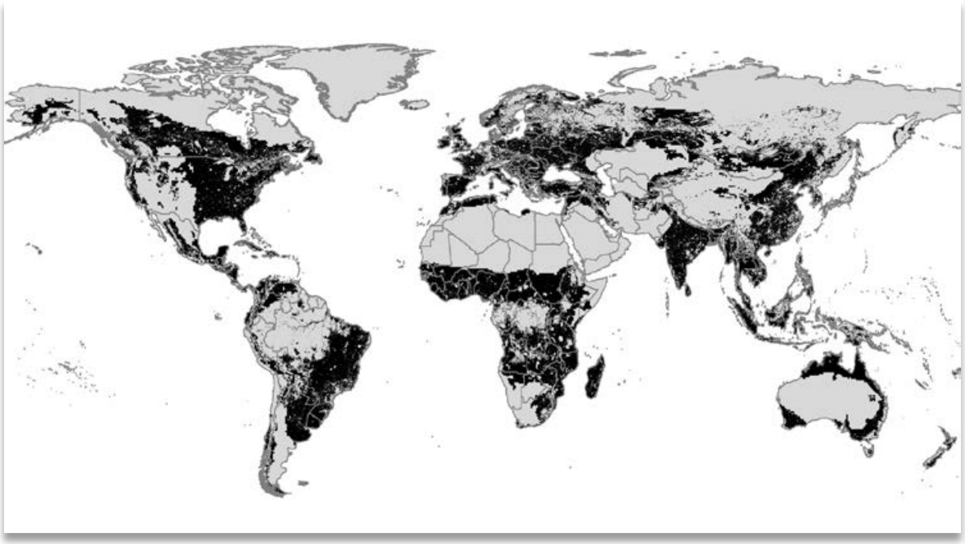
Development of EU GHG emissions [Gt CO_2e]



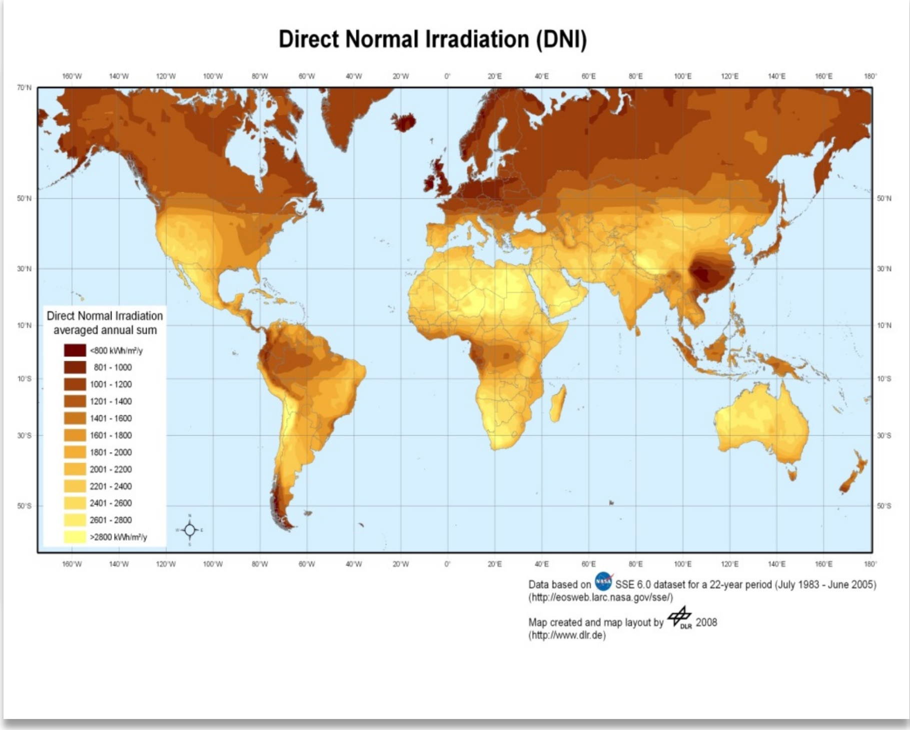
1 Large efficiency improvements are already included in the baseline based on the International Energy Agency, World Energy Outlook 2009, especially for industry
2 Abatement estimates within sector based on Global GHG Cost Curve
3 CCS applied to 50% of large industry (cement, chemistry, iron and steel, petroleum and gas, not applied to other industries)

SOURCE: www.roadmap2050.eu

Biomass and Solar Energy need to contribute strongly as a source for aviation fuels

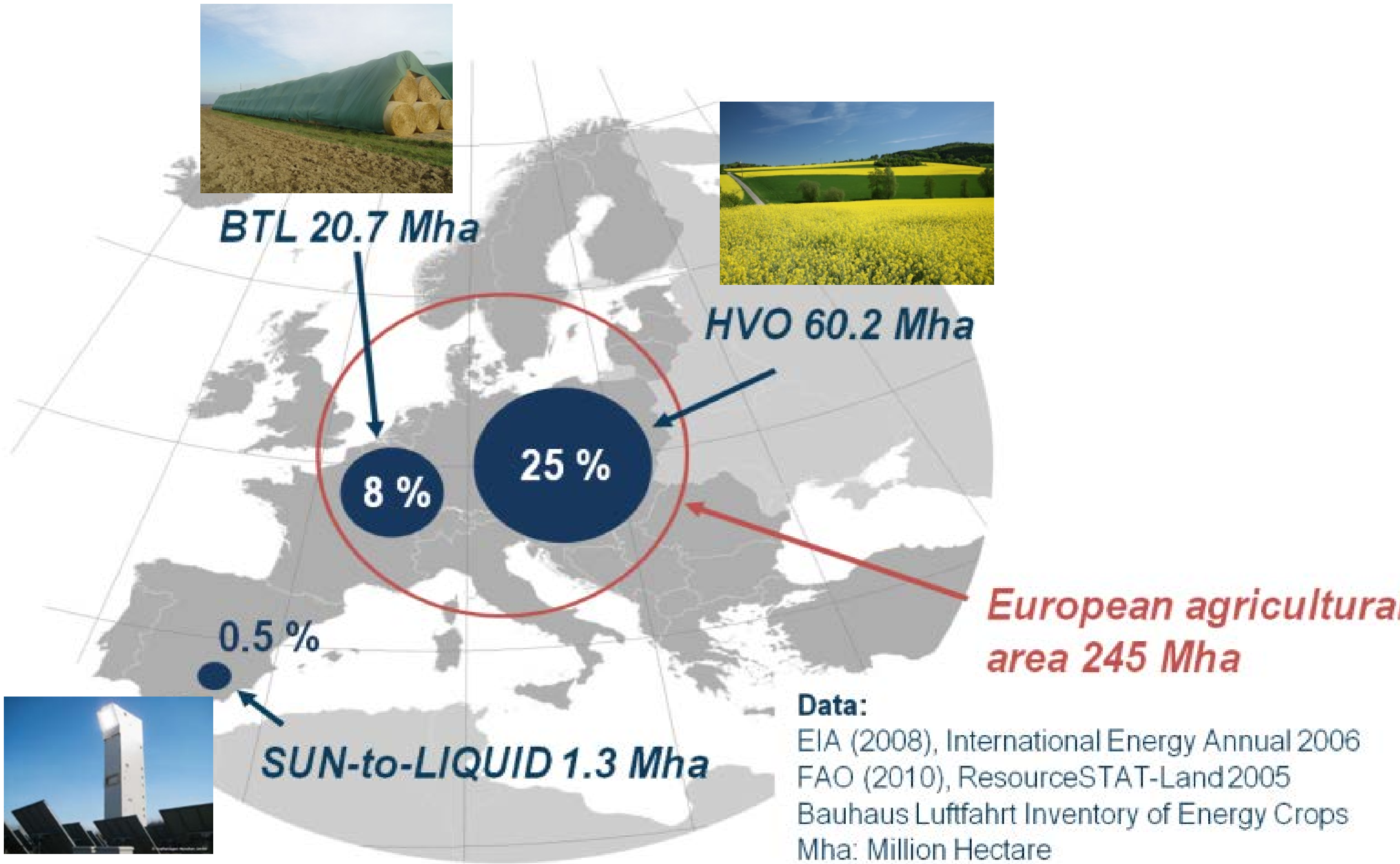


Area used for agriculture*



*F. Riegel, Das nachhaltige Potenzial von Flüssigkraftstoffen aus Biomasse: Eine globale Abschätzung auf der Basis von hochaufgelösten Geodaten, Ph.D. thesis, Ludwig-Maximilians-Universität Munich, submitted for evaluation, 2015

Fraction of E27 agricultural surface to provide European Kerosene demand of 2005:



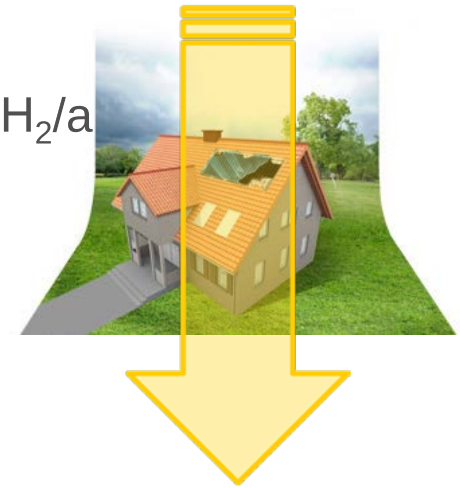
Data:
EIA (2008), International Energy Annual 2006
FAO (2010), ResourceSTAT-Land 2005
Bauhaus Luftfahrt Inventory of Energy Crops
Mha: Million Hectare

DLR

Bio-Artificial Photosynthesis

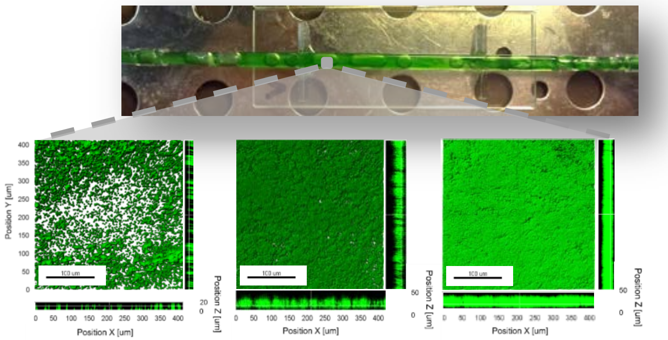
25.000 kWh per year*

* estimated based on EnEV 2007



→ 4000 kg H_2/a
→ 200 m²

Highlight: Phototrophic *Synechocystis* sp. PCC 6803 Biofilm



Scope and Potential

- Low-cost routes (~1 €/kg) towards H_2 and chemicals using photo-catalytic microbes
- Theoretical efficiencies up to 9% possible
- Stability by regeneration

Challenges

- Coupling of productive biocatalysis to photosynthesis → high risk, high gain
- Understand kinetics, stoichiometry, and photocatalytic reaction mechanisms
- Design of a highly active photosynthetic H_2 producer

Milestones

- Demonstration of photoactive catalytic biofilm in continuous reactor setup
- Quantification of parameters that control operation of photosystems *in vivo*

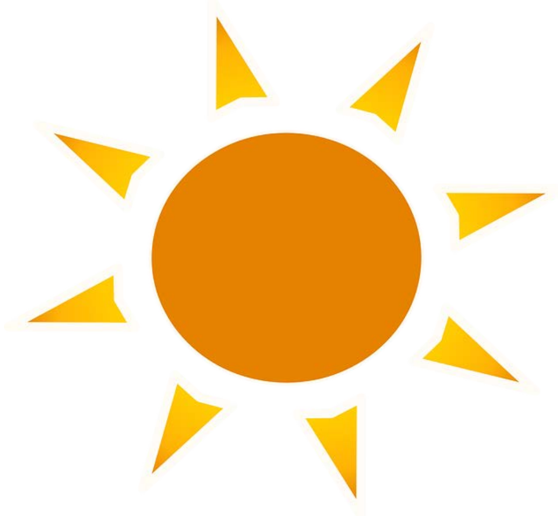
Trends in Biotechnol., **30**:453 (2012)
Appl. Environ. Microbiol., **77**:1563 (2011)

Solar Fuels

CO_2 reduction by replacing fossil feedstock and utilisation of CO_2 as feedstock

Carbon dioxide (CO_2)

Water (H_2O)



Synthesis gas (H_2 + CO)

e.g. Fischer-Tropsch-Plant

Sustainable synthetic petrol,
diesel, kerosene
hydrogen, methanol,
(fertilisers, polymers)…

Solar Electrolysis

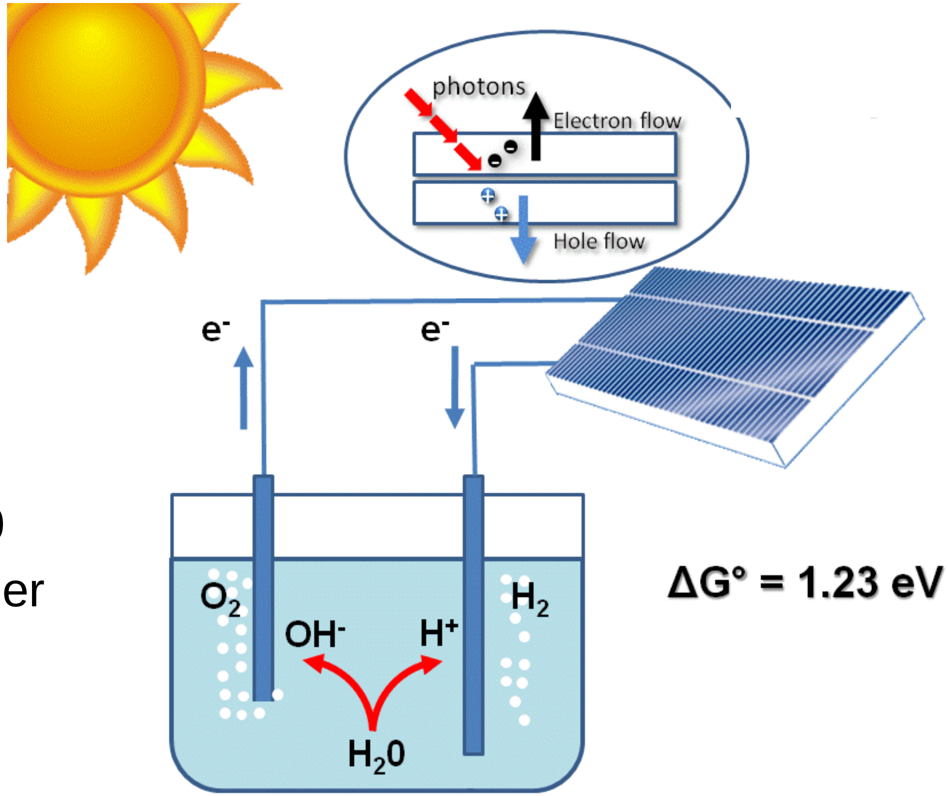


Figure 1

Status of Electrolysers

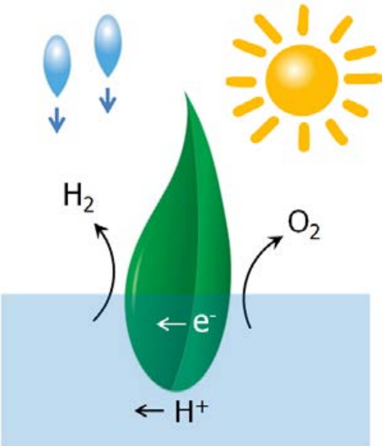
- Used in chemical industry under constant load condition
- Not optimized for operation with intermittent load
- Efficiency ~ 70- 75% today with potential to reach 82% in 2030
- Lifetime estimation of 60'000 h under constant load, no experience with intermittent load
- Investment costs
  Alkaline ~1100€/kW (2014); 600 €/kW (2025)
  PEM ~2100€/kW (2014); 870 €/kW (2025)

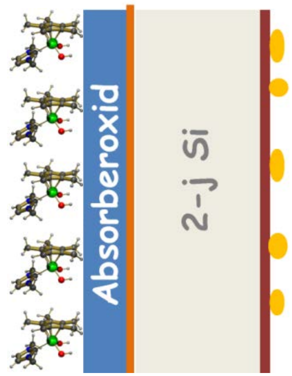
Cost of Hydrogen from Renewables (German Mix)

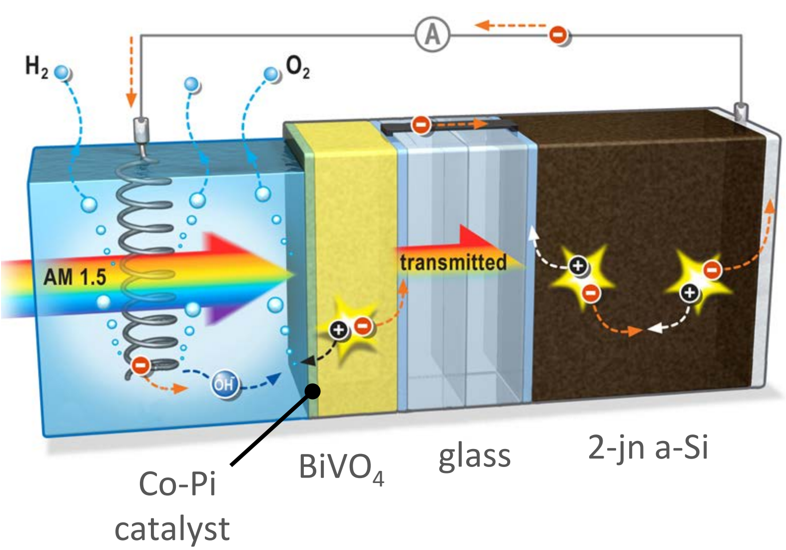
- **2012:** Alkaline: 5€/kg; PEM 7.6€/kg
- **2030:** Alkaline: 3,3 €/kg; PEM 2,7 €/kg

Data from: Development of Water Electrolysis in the European Union; Final Report for Fuel cells and hydrogen Joint undertaking (2014)

Photoelectrochemical Routes







Highlight: 4.9% efficient device

Nat. Commun. 4 (2013) 2195

Scope and Potential

- Integration of light absorption and catalytic functionalities
- Strong synergy with Topic 1 (PV)
- Efficiencies can approach PV (10-20%)

Challenges

- Develop stable light absorbers and efficient low-cost, earth-abundant catalysts
- Understand and control interfaces
- Scale-up to mini-modules (η>5%)

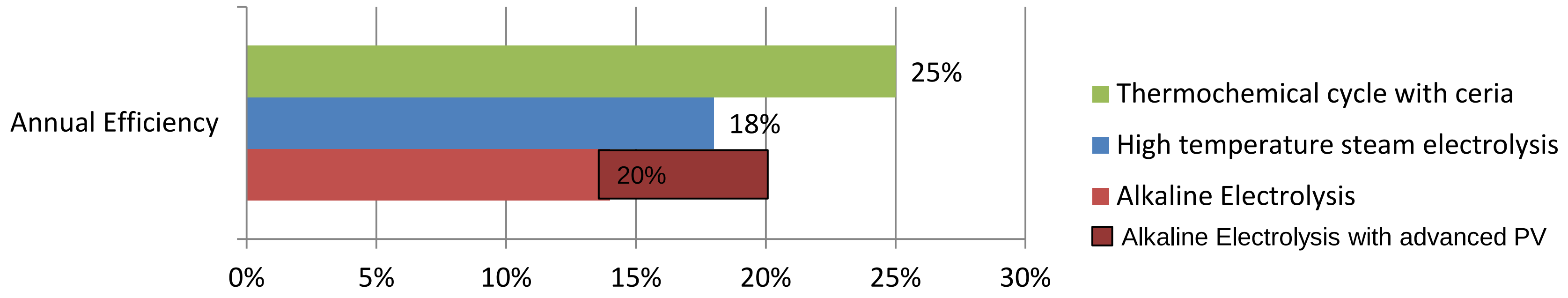
Milestones

- Novel complex oxides with E_g < 2.2 eV
- Demonstrate 8% solar-to-H_2 efficiency
- Less than 10% decrease in 200 hours

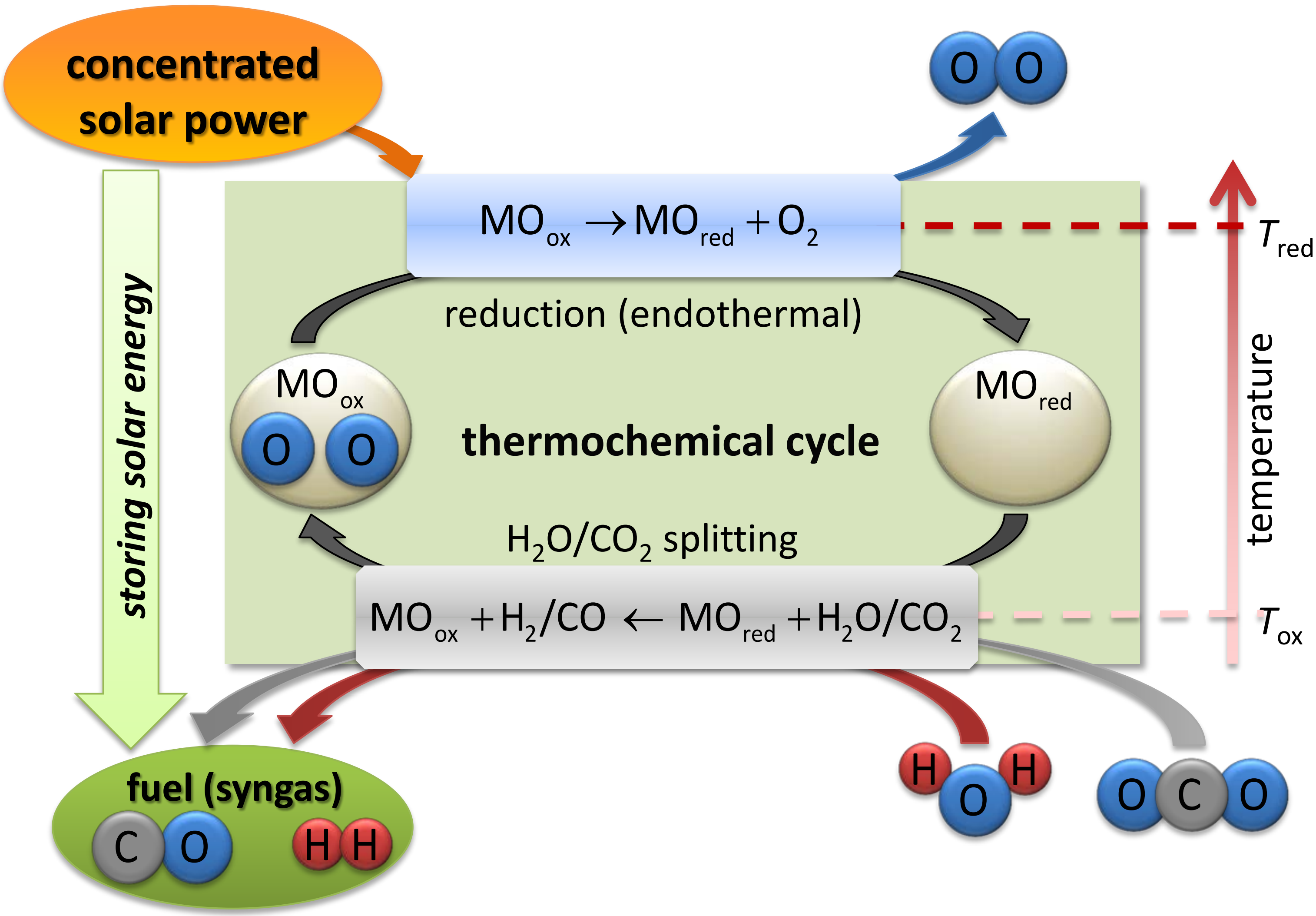
Efficiency Comparison vs. Benchmark

Process	temperature of the chemical reaction	Solar interface receiver temperature
Alkaline Electrolysis	25°C	Solar PV
High temperature steam electrolysis	850°C	Future solar tower 1200°C
Thermochemical cycle with ceria	1500 / 1150°C	Future solar dish 1500°C

*G.J. Kolb, R.B. Diver SAND 2008-1900 / N. Siegel et al. I&EC Research May 2013

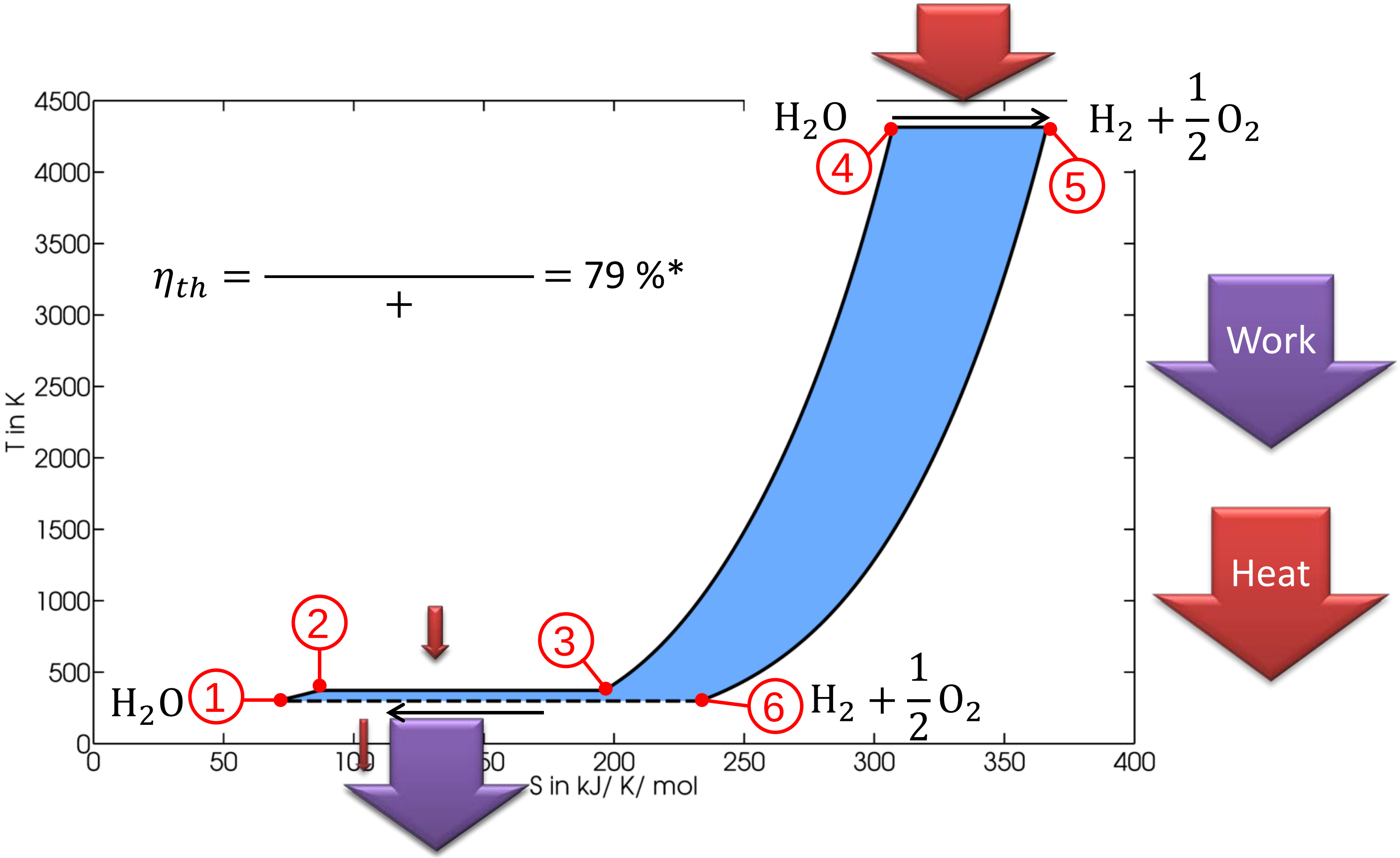


Thermochemical cycle



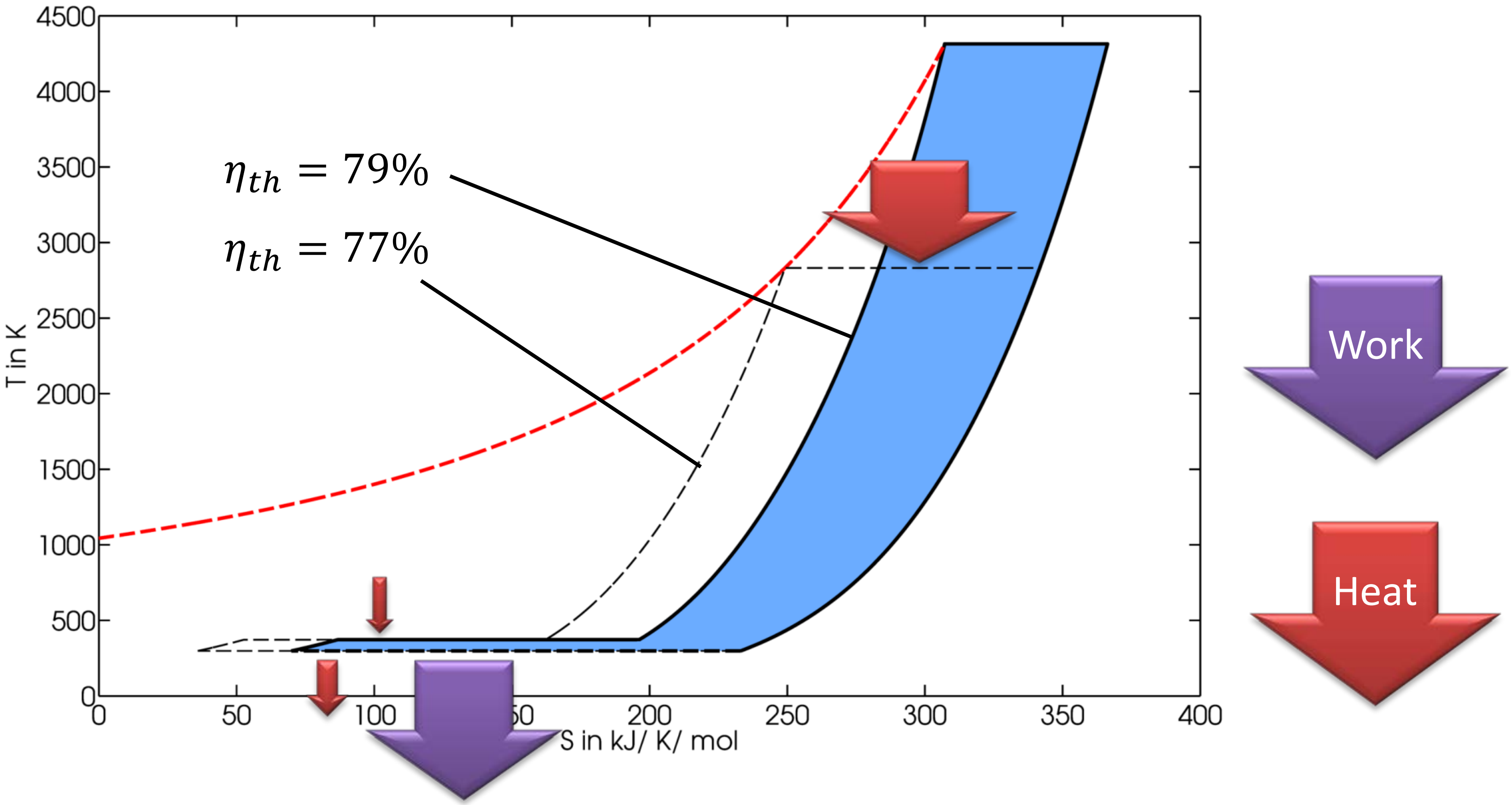
$$dQ_{rev} = T\,dS$$

Direct Water Splitting: T–S Diagram

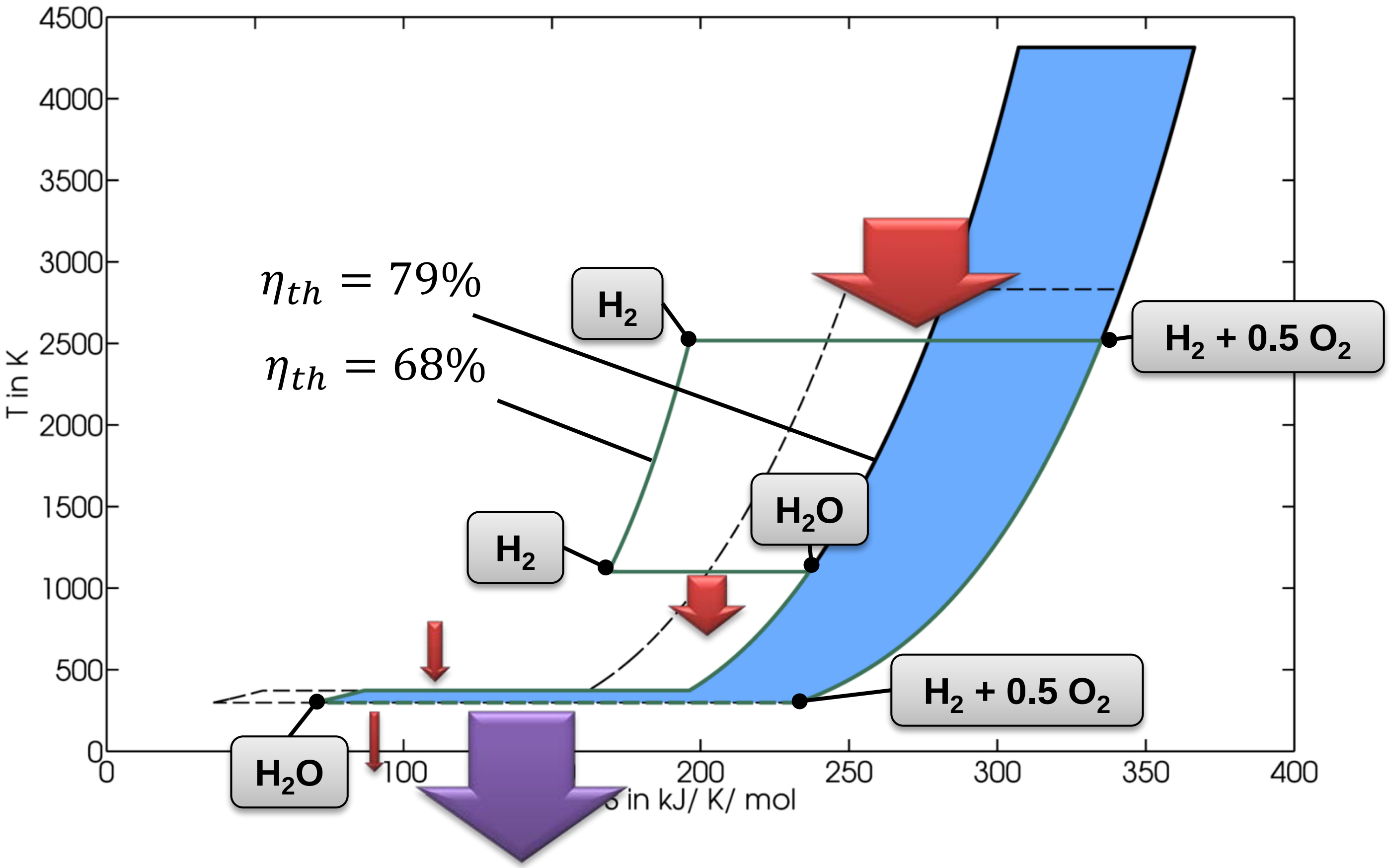


* Including ideal heat recovery

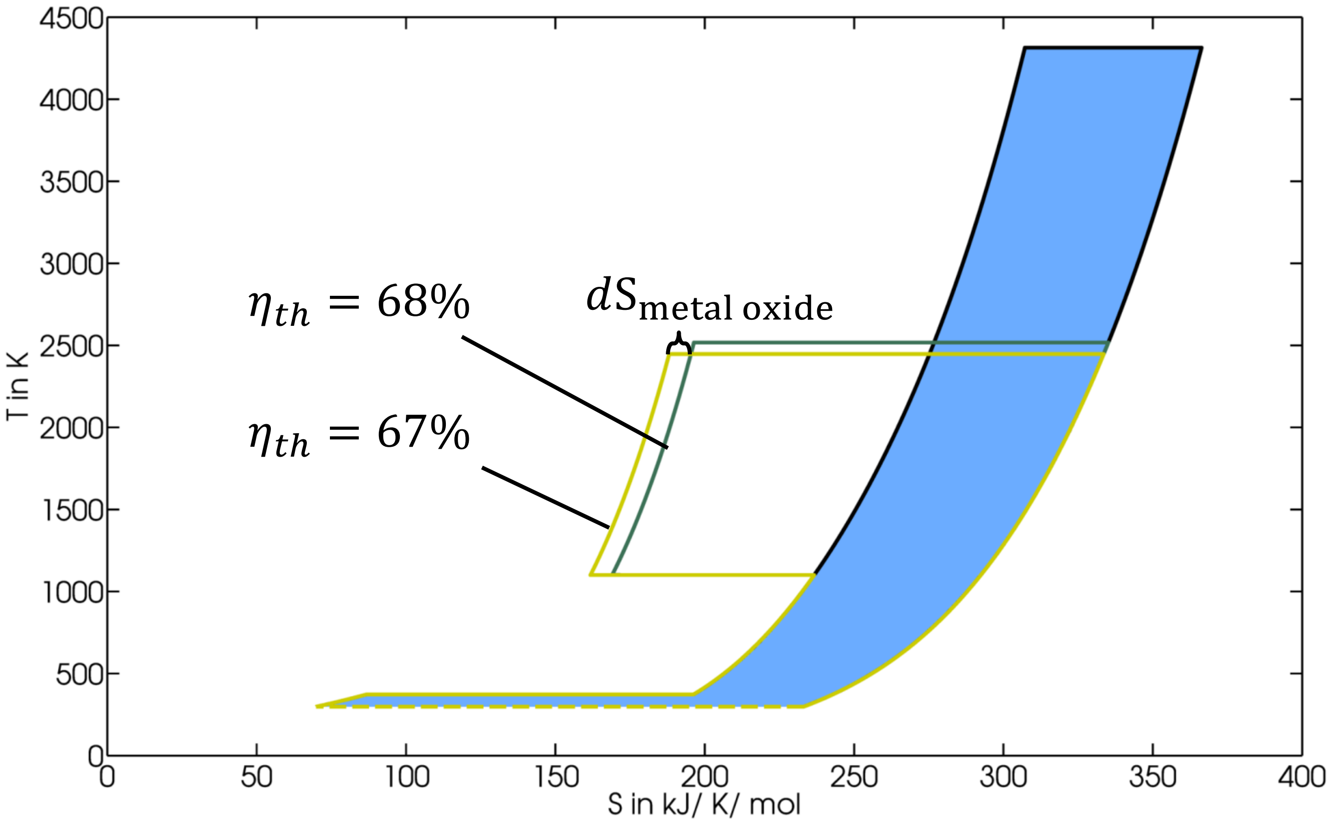
Direct Water Splitting: Equivalent Process



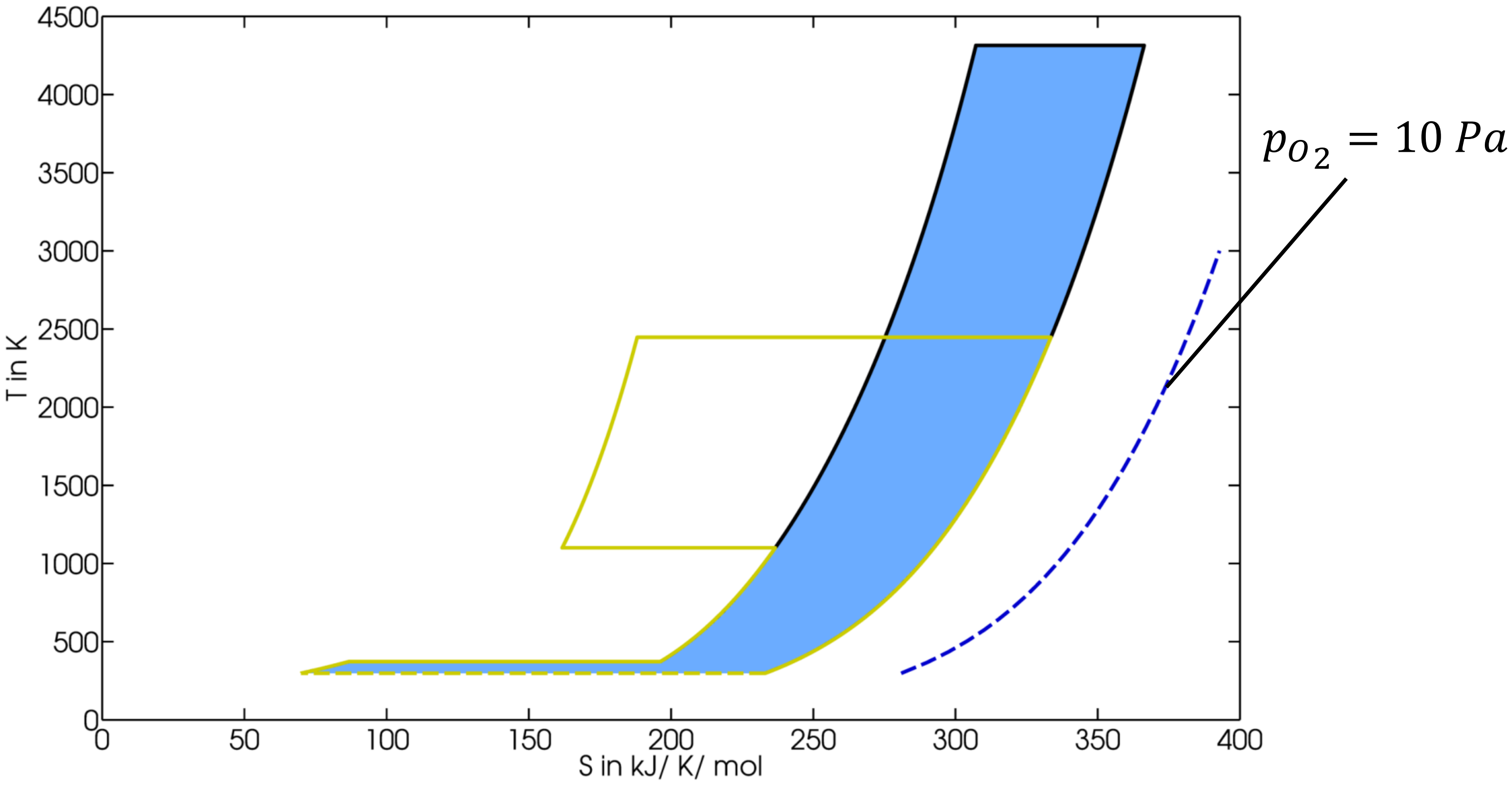
Two Step – Gas Phase Only



Two Step – Influence of Metal Oxide



Two Step – Influence lower (partial) pressure



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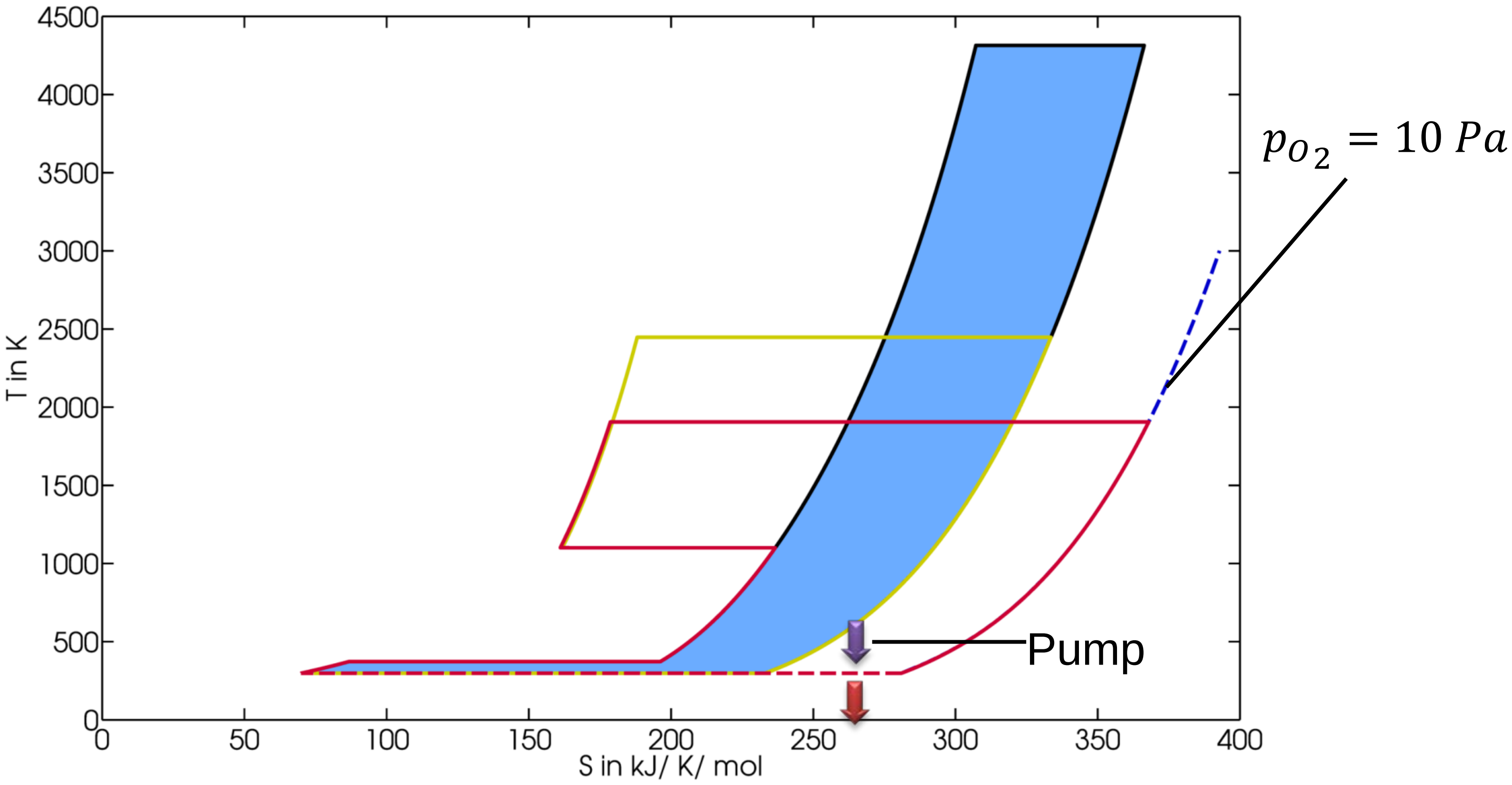
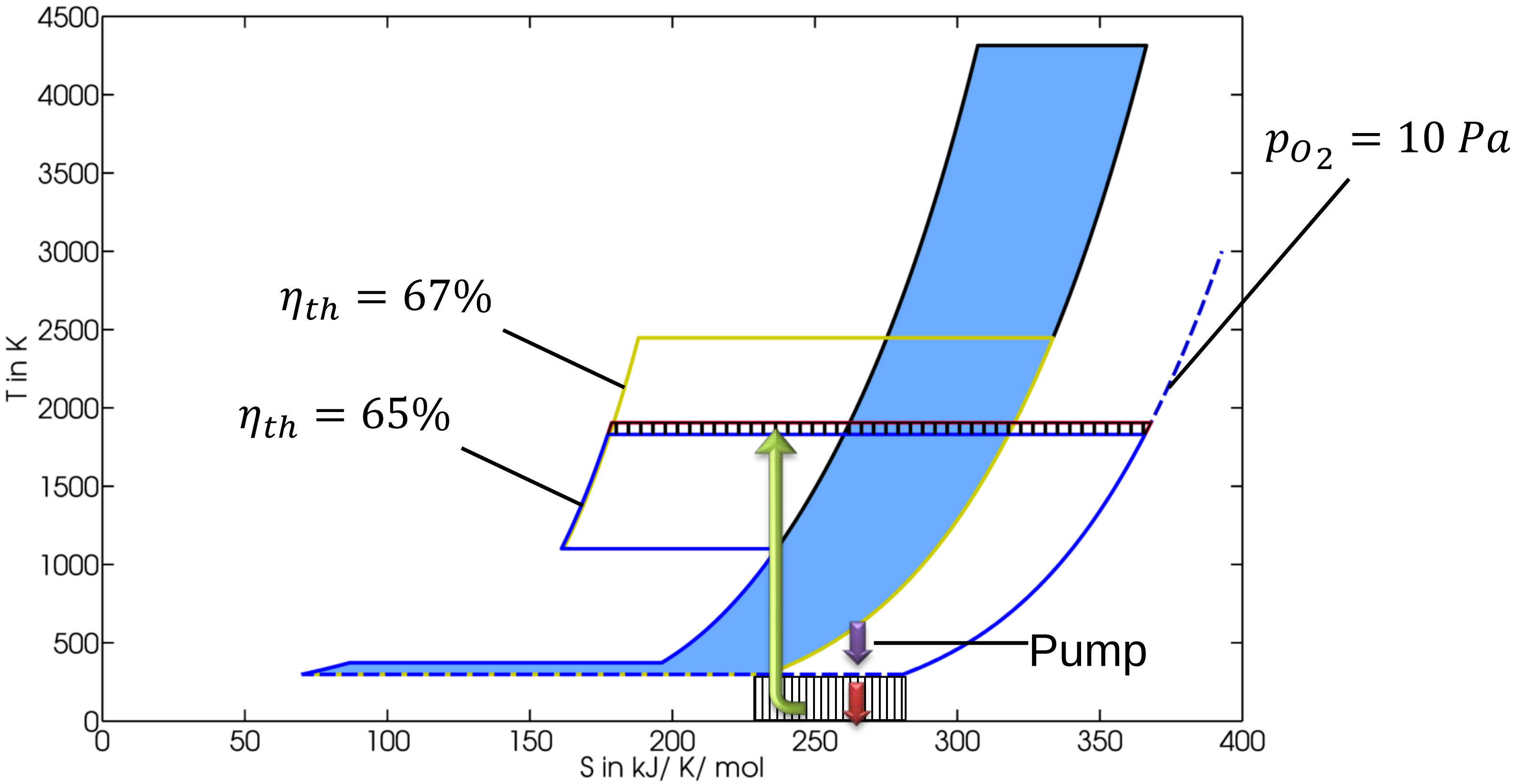
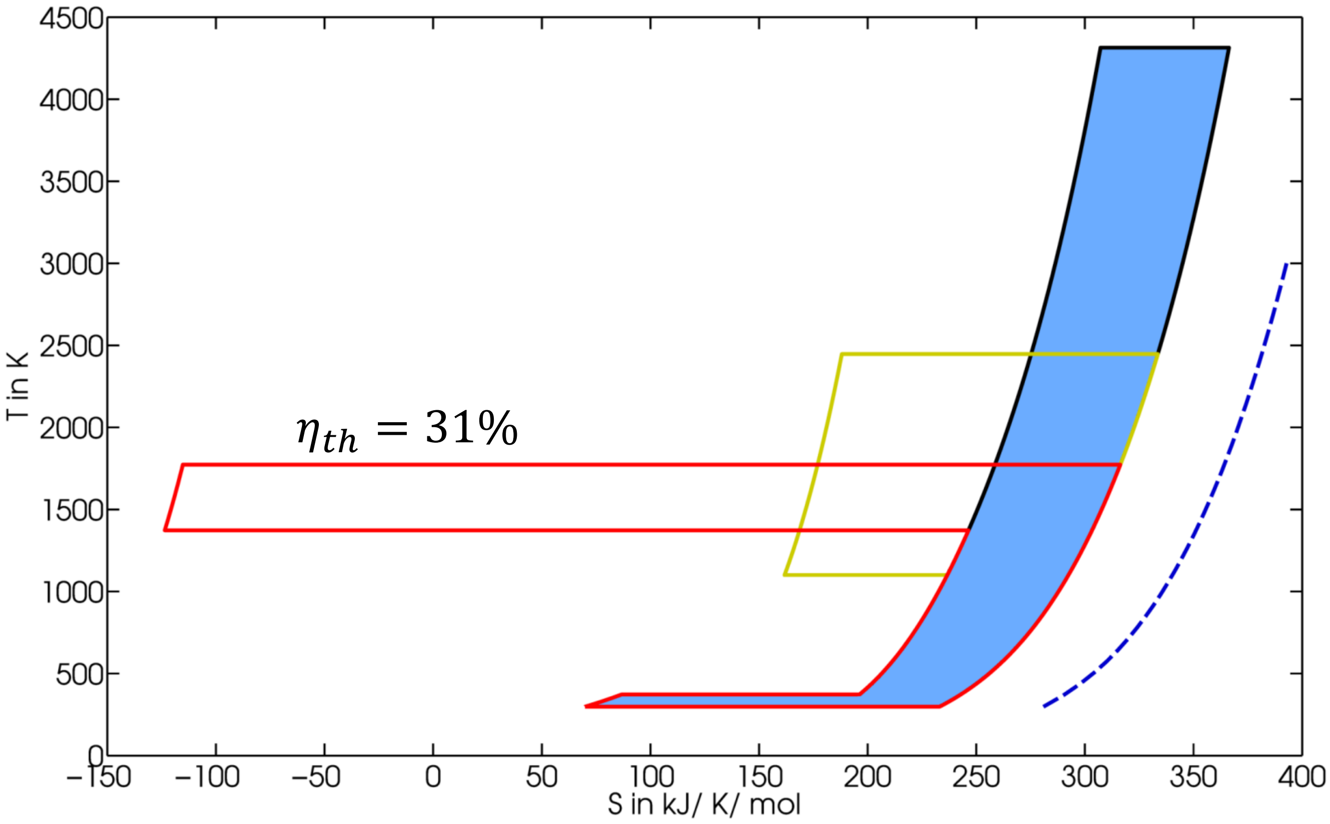


Two Step – Influence lower (partial) pressure



Two Step – Temperature levels: 1500/ 1100 °C



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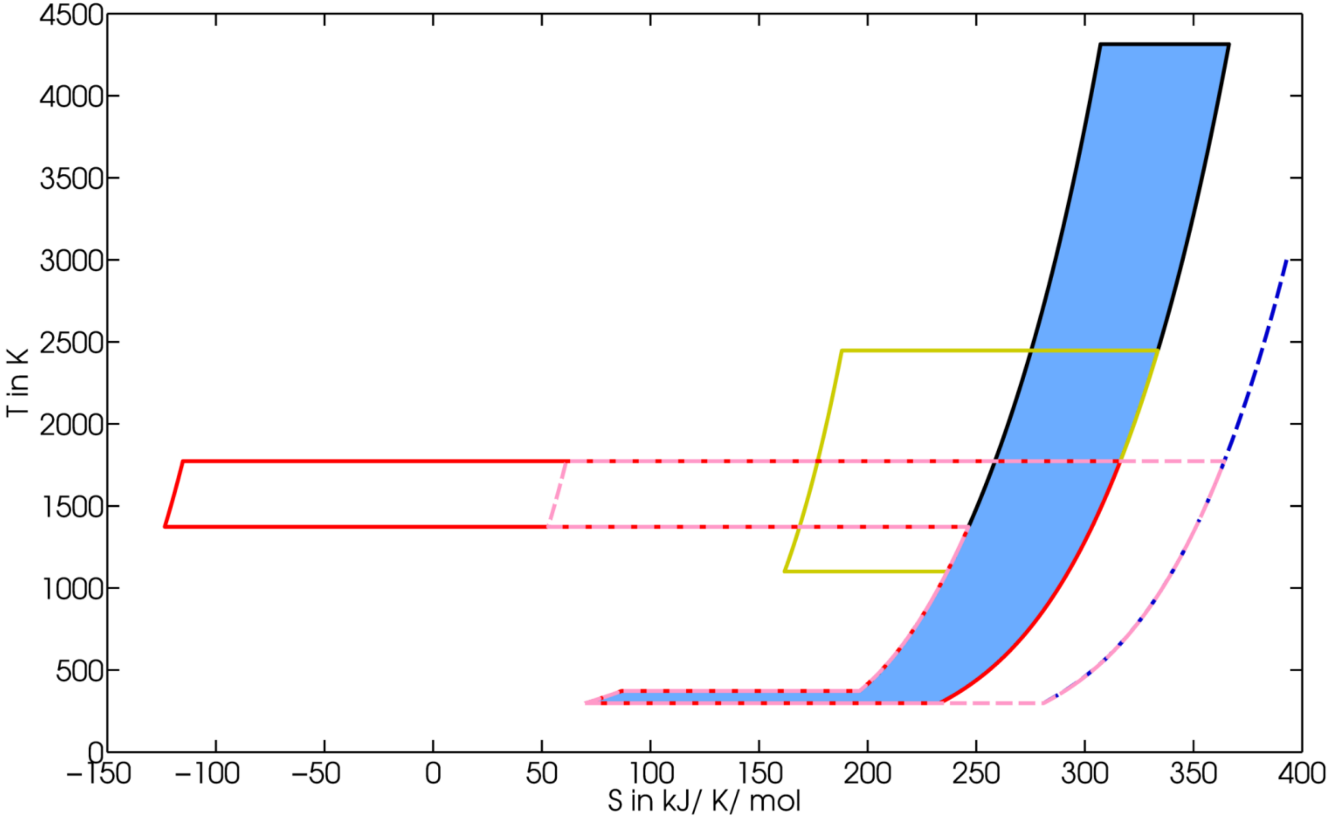
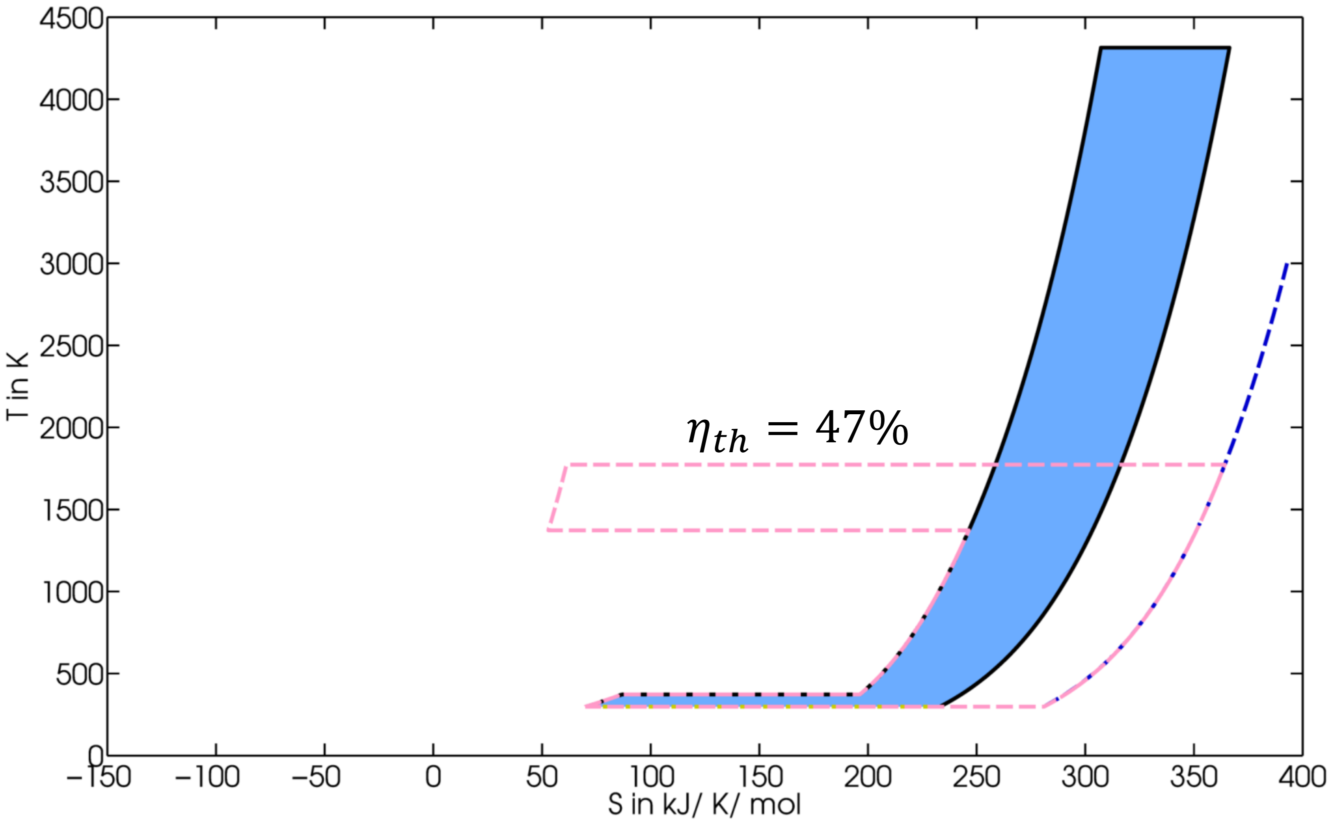


DLR

Two Step – Temperature levels: 1500/ 1100 °C

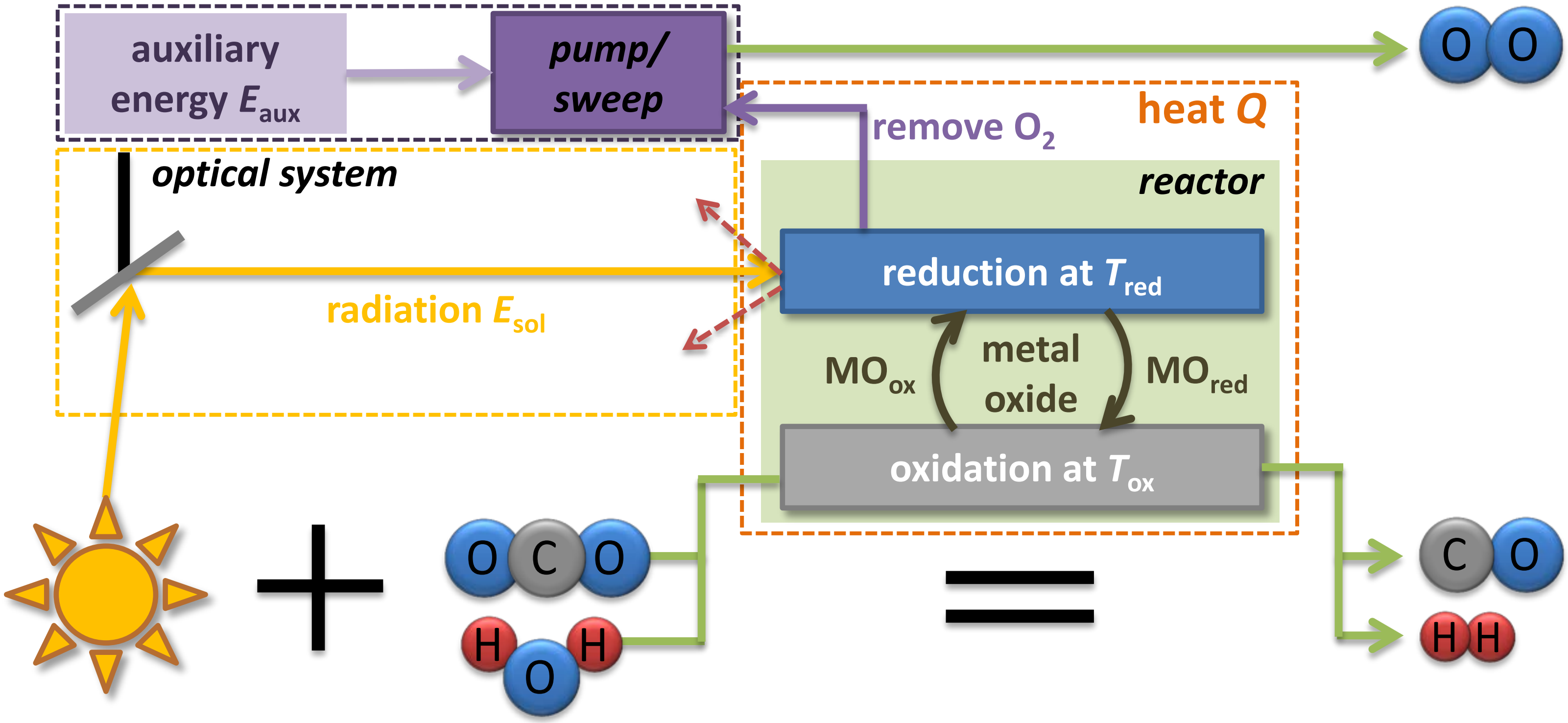


Conclusions from Thermodynamic Analysis

- T-S Diagrams provide vivid representation of two step thermochemical cycles

- Efficiency analysis possible
  - All rejected heat at high temperatures reduces efficiency
  - Low oxygen partial pressure may facilitate the process (temperature!) and increase efficiency, but electricity needs to be provided
  - Equal temperature of oxidation and reduction is possible, but very low pressure would be necessary

Challenges of the entire process



Production of CO_2-neutral renewable fuels through solar-driven thermochemical cycles ($ + η)

material side

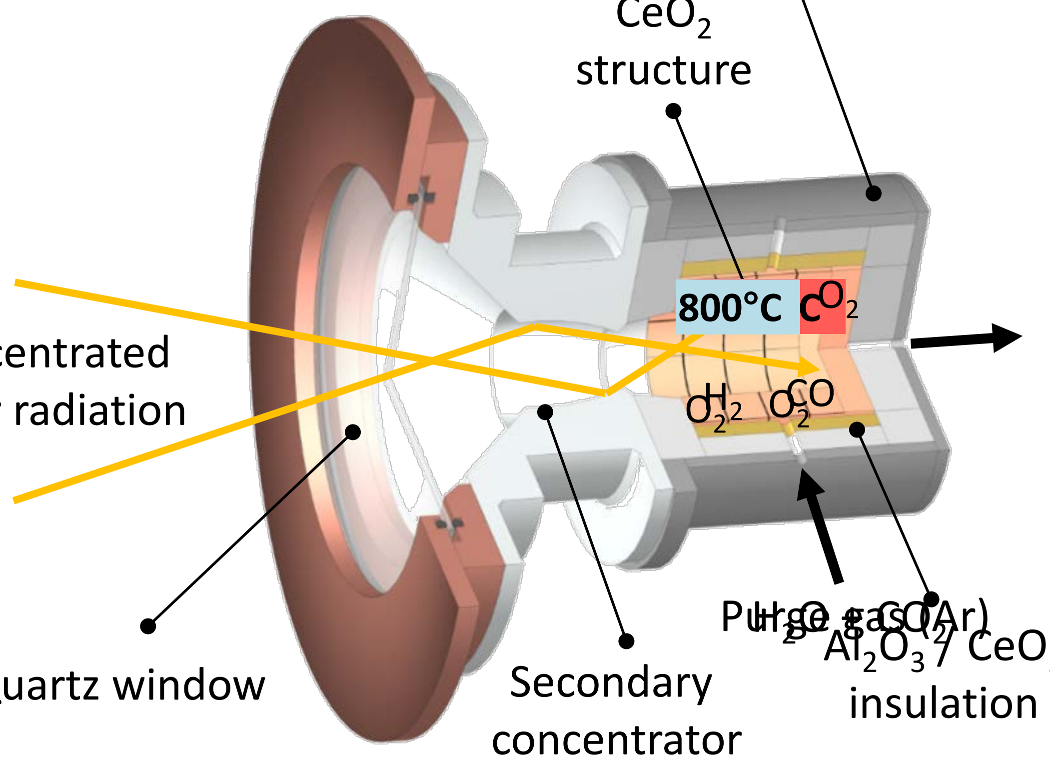
- Determination of atomic mobilities in the redox materials
- Identification of methods to enhance long-term stability
- Improvement of hydrogen/CO yield per cycle and conversion rate

process side

- Analysis and modelling of heat transfer mechanisms in the solar receiver
- Solar heat incorporation: Matching rates of chemical reaction and heat transfer
- Analysis and optimization of transport (conversion rates and residence times)

v) Experimental validation of the process

CeO_2 Red-Ox Reactions in Solar Reactor



1. Reduction:

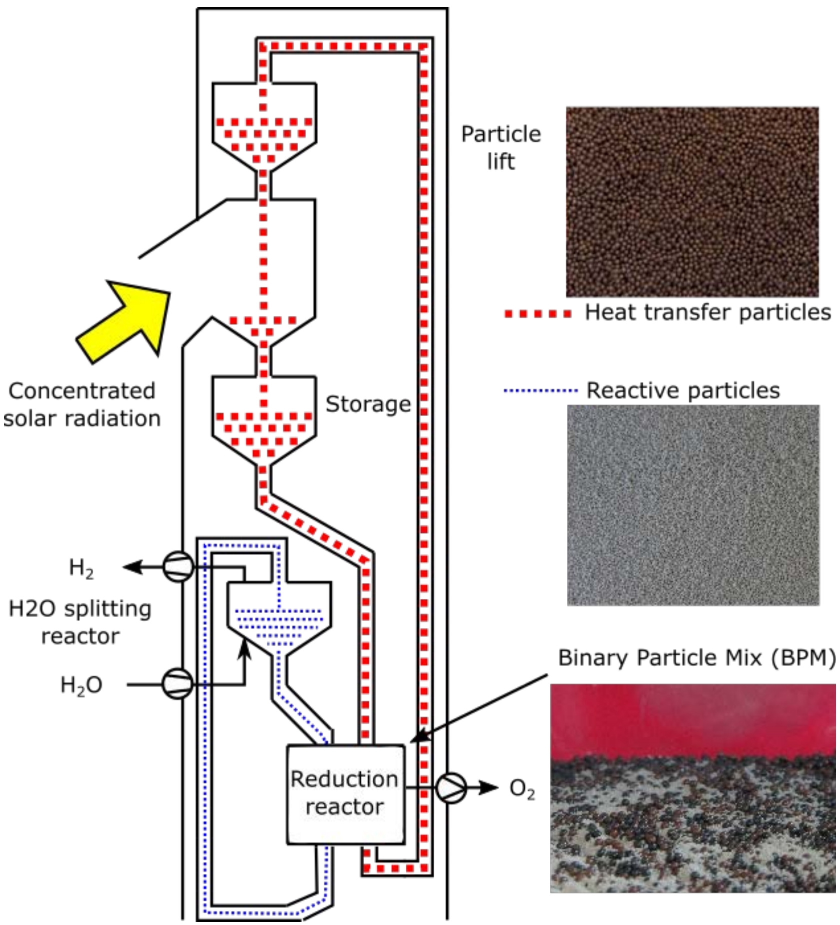
$$CeO_2 \rightarrow CeO_{2-\delta} + \frac{\delta}{2} O_2$$

2. Oxidation:

$$CeO_{2-\delta} + \delta H_2O \rightarrow CeO_2 + \delta H_2$$

$$CeO_{2-\delta} + \delta CO_2 \rightarrow CeO_2 + \delta CO$$

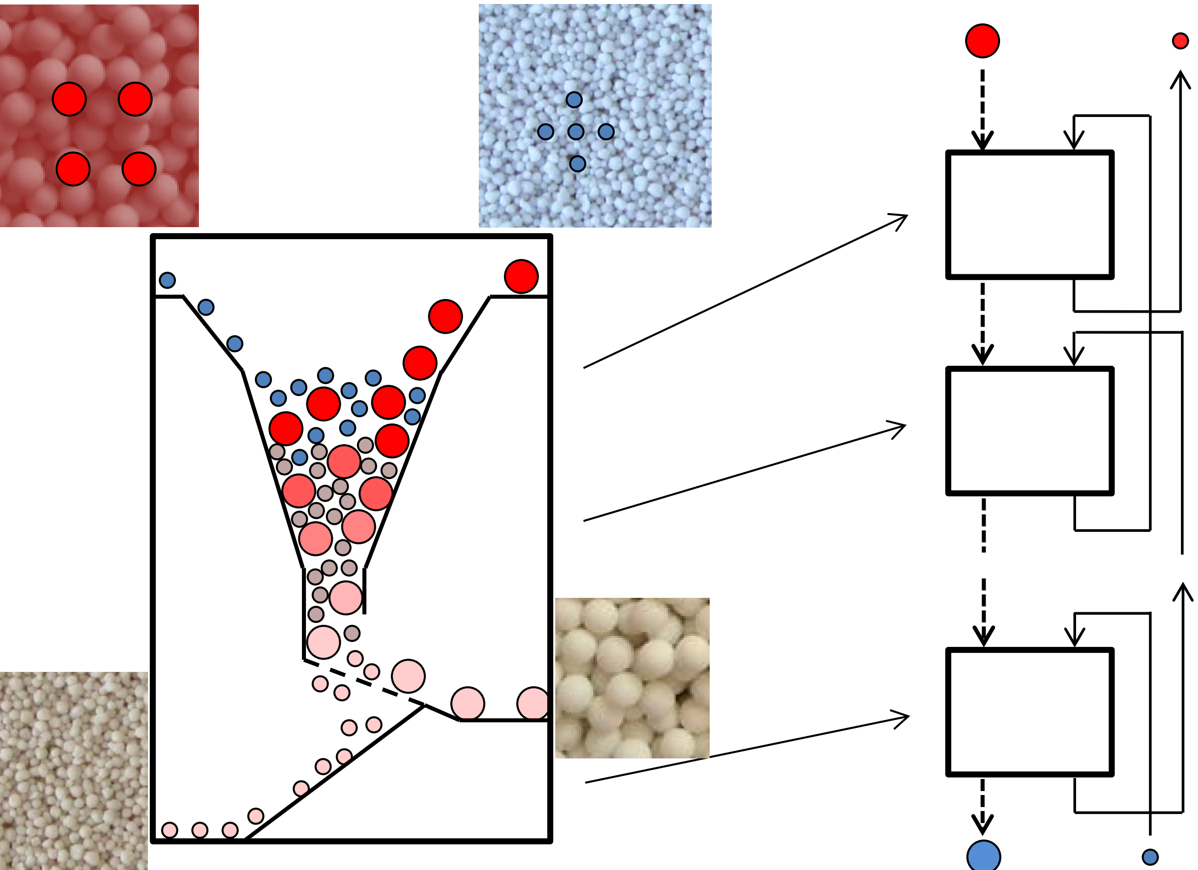
New Process Concept – Particle Based, Indirect



- Heat transfer particles
- Reactive particles
- Binary Particle Mix Reactor
- Decoupling of solar integration from reduction reaction
- Optimized particles for absorption
- Windowless receiver
- Solid phase heat recovery

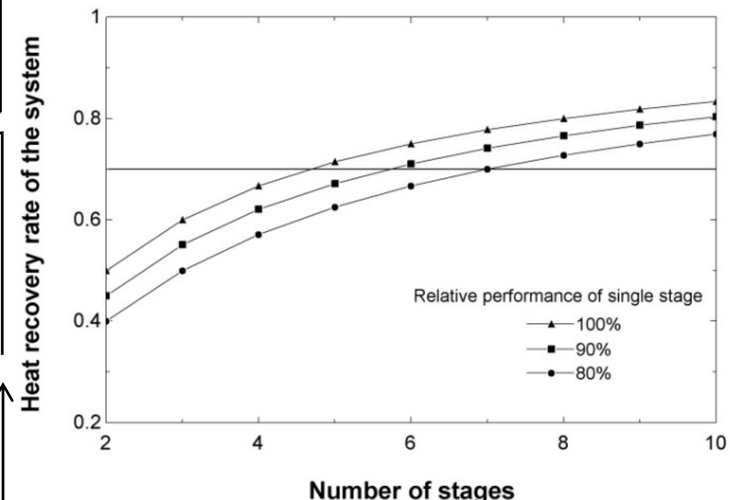
Brendelberger, S., Sattler, C., Concept Analysis of an Indirect Particle-Based Redox Process for Solar-Driven H_2O/CO_2 Splitting, Solar Energy, 113 (2015) 158-170.

Solid Phase Heat Recovery
Particle – Particle Heat Transfer



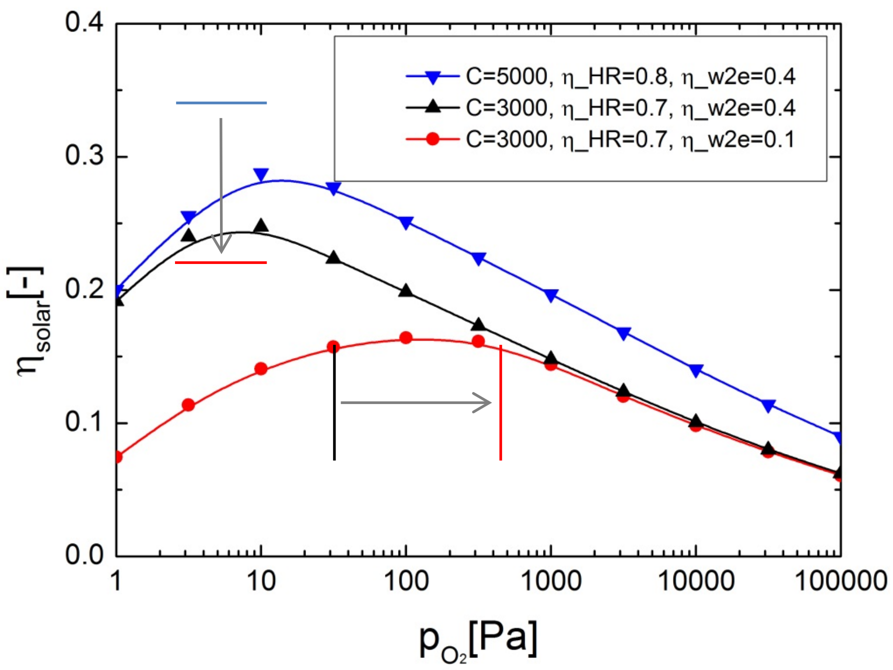
Co-current heat exchanger

Quasi counter-current heat recovery system



Felinks, J., Brendelberger, S., Roeb, M., Sattler, C., Pitz-Paal, R., Heat Recovery Concept for Thermochemical Processes Using a Solid Heat Transfer Medium, Applied Thermal Engineering, 73 (2014) 1004-1011

Performance analysis



Analysis with different assumptions (C, η_HR, η_w2e)

Use of waste heat to compensate auxiliary power demand is crucial

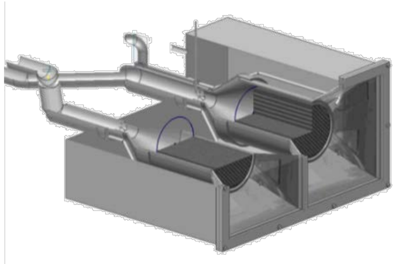
Pumping power requirements limit minimum pO2

Below 100Pa pumping power demand becomes prohibitive

Brendelberger, S., Sattler, C., Concept Analysis of an Indirect Particle-Based Redox Process for Solar-Driven H_2O/CO_2 Splitting, Solar Energy, 113 (2015) 158-170.

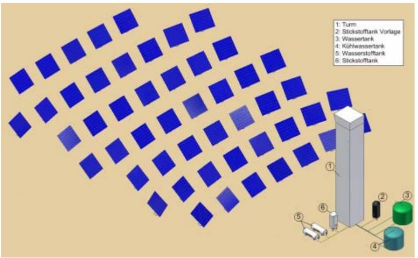
Development of such a Technology needs several scaling steps

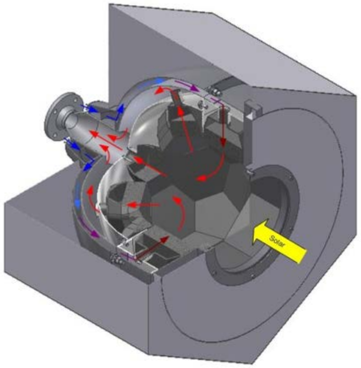
Hydrosol I
2002 – 2005
< 10 kW



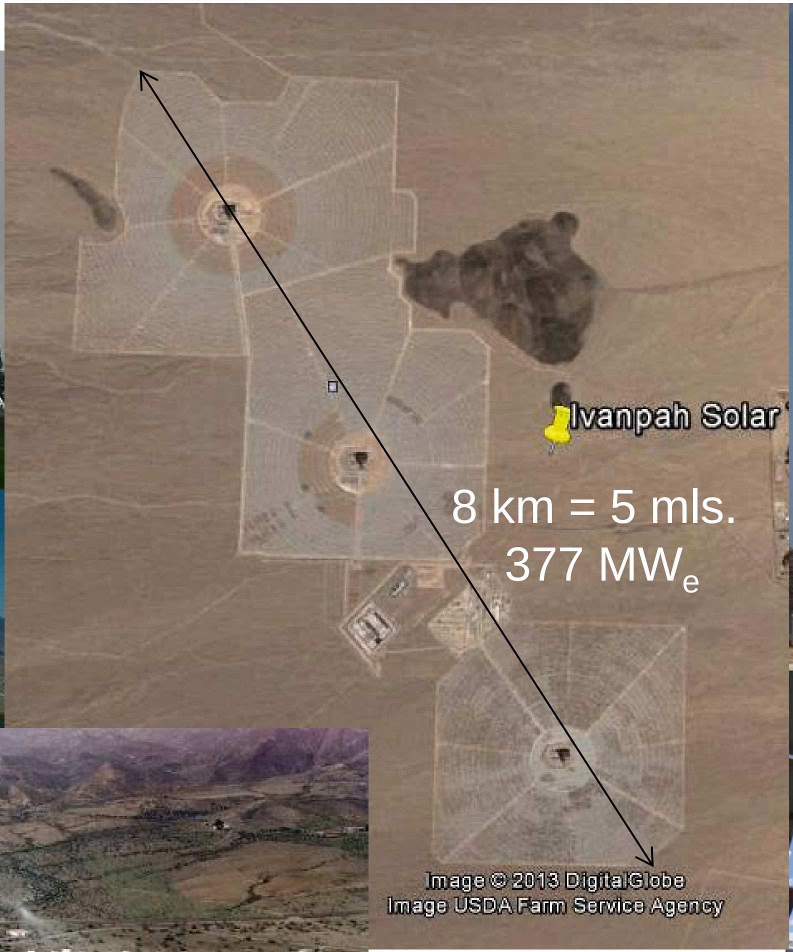
Hydrosol II
2006 – 2009
100 kW

Hydrosol 3D
2010 – 2012
1 MW





Application target is centralized production in GW scale



http://www.ivanpahsolar.com/

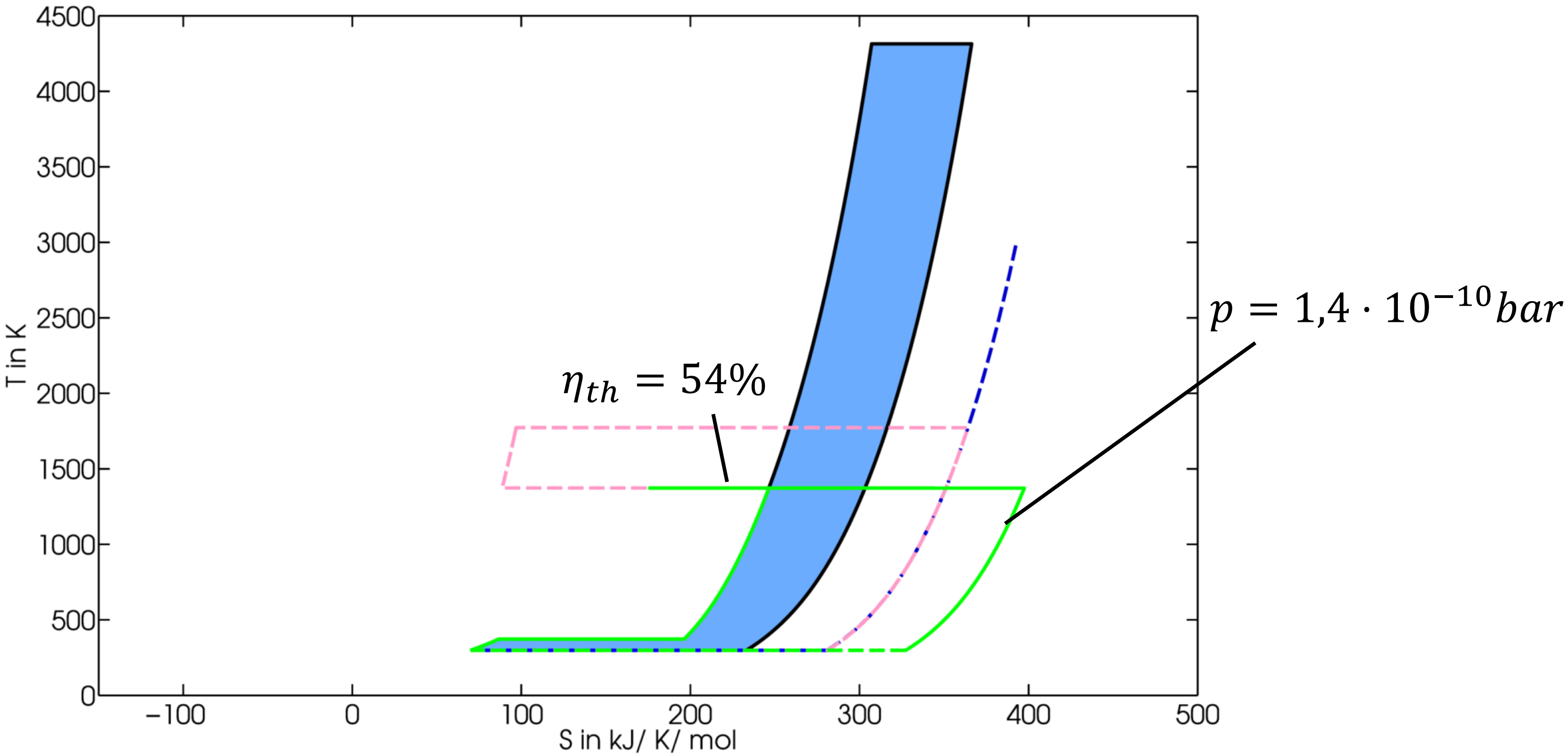
-PS10, Ivanpah, Torresol
-PSA CRS, CESA-1,
-Solar-Two, Daggett,

Conclusion

- Land requirements for solar fuel application are at least one order of magnitude smaller than for biomass applications.
- In solar fuel applications there is no competition with alternative land use
- Solar electrolysis is a young technology with first commercial projects
- To reduce cost adaptation of current industrial electrolyser designs is required so that a mature technology status can be reached until 2025
- Solar photo-electrochemistry, artificial photosynthesis and thermochemical cycles are technology options that may overcome efficiency and cost constraints of solar electrolysis, thus allowing to reach lower fuel cost.
- All options are in a research stage and no commercial products are available today.
- The thermochemical approach is considered to be the most advanced concept
- A first commercial demonstration is expected around 2025

Thank you very much for your attention!

Two Step – Red and Ox at one Temperature?



If pumping power provided solar (η = 15%), efficiency decreases to 30 %